# PERCHLORIC ACID

(CAS 7601-90-3 ; $HClO_4$)

## SCOPE OF THE DOCUMENT

This document focuses on the hazards of perchloric acid. The toxicity, fire, explosion and reactivity hazards of perchloric acid are described. Information relevant to the workplace is emphasized. Special attention is given to the main hazard presented by perchloric acid.

# PERCHLORIC ACID - CHEMICAL HAZARD SUMMARY NO. 35

Each document produced by CCOHS undergoes several stages of review. As part of this review, representatives from government, employers, and labour are requested to comment on draft copies of CCOHS documents for technical accuracy and usability.

Although every effort is made to ensure accuracy and completeness of the information, it is understood that CCOHS makes no warranty as to the accuracy or completeness of such information and assumes no liability for any damages or loss suffered as a result of any inaccuracy or incompleteness therein.

This publication is available in both official languages.

Cette publication est disponible dans les deux langues officielles.

CCOHS NUMBER C87-15E
ISBN 0-660-12661-3
DSS CATALOGUE NUMBER CC273-4/87-15E

Published 1987

Additional copies available upon request.

---

250 Main Street East
Hamilton Ontario
L8N 1H6
(416)572-2981
Telex 061-8532

CCOHS/CCHST

# TABLE OF CONTENTS


I. MAIN HAZARD . . . . . 1

II. OCCUPATIONAL EXPOSURE . . . . . 1

III. HEALTH HAZARDS . . . . . 1

Effects of Short-Term Overexposure in Humans . . . . . 1
Effects of Long-Term Overexposure in Humans . . . . . 2
Toxicity Data in Animals and Laboratory Tests . . . . . 2

IV. FIRE AND EXPLOSION HAZARDS . . . . . 3

V. CHEMICAL REACTIVITY . . . . . 3

VI. EXPOSURE LIMITS . . . . . 4

VII. EXPOSURE CONTROLS . . . . . 4

Protective Clothing . . . . . 4
Respiratory Protection . . . . . 5

VIII. STORAGE AND HANDLING . . . . . 5

IX. FIRST AID . . . . . 6

Inhalation . . . . . 6
Eye Contact . . . . . 6
Skin Contact . . . . . 6
Ingestion . . . . . 6
General . . . . . 6

X. FIRE FIGHTING . . . . . 7

XI. CLEAN-UP AND DISPOSAL . . . . . 7

XII. REFERENCES . . . . . 8




CCOHS/CCHST

# I. MAIN HAZARD

There are two main hazards of perchloric acid. 1. It is a strong acid. At room temperature, it can severely irritate or burn all tissues it contacts. 2. It is an extremely strong oxidizing and dehydrating agent (removing water from substances) when heated to temperatures above 160°C (320°F)[1]. As an oxidizing agent, perchloric acid gives off oxygen when heated with other chemicals. The supply of oxygen from perchloric acid can cause fires to burn more intensely or can cause violent chemical reactions.

# II. OCCUPATIONAL EXPOSURE

This document deals mainly with the usual commercial forms of perchloric acid which contain 60-72% acid in water.

Perchloric acid can be made up in solutions containing more than 72% acid. Even anhydrous (pure) 100% perchloric acid can be prepared. Concentrations of 85% and above absorb water readily and are unstable even at room temperature[2]. These materials should only be used by trained workers[3].

Perchloric acid is used in the manufacture of explosives and rayon, in electroplating and polishing, as a battery electrolyte, as a laboratory reagent and in biological analyses (wet combustion).

The principal routes of exposure to perchloric acid are inhalation of vapours and mists, and skin and eye contact with the liquid form.

General information on routes of exposure is available in the CCOHS document "How Workplace Chemicals Enter the Body."[4]

# III. HEALTH HAZARDS

## Effects of Short-Term Overexposure in Humans

There is little specific information available on the health effects of exposure to perchloric acid. Nevertheless, the potential health hazards of this material are predictable - they are primarily due to its corrosive nature. The effects of exposure to perchloric acid and other corrosive materials depend mainly on the concentration and the duration of exposure.

Inhalation

Exposure to vapours and mists can cause a burning sensation in the nose and throat, and lung irritation with coughing. Prolonged exposure can cause severe coughing, nausea and vomiting[5,6].

Eyes

Exposure to perchloric acid vapours and mists can cause eye irritation and possibly burns. Splashes of commercial grade perchloric acid cause severe burns which may result in permanent eye damage if not treated promptly.

Skin

Contact with perchloric acid solutions causes irritation or corrosion of the skin. If not rinsed off quickly with water, commercial grade solutions will cause severe burns.

Ingestion

Swallowing perchloric acid is unlikely in the workplace. Swallowing commercial grade solutions causes burns to the mouth and digestive tract. There is pain in the stomach, difficulty breathing, nausea, vomiting, diarrhea, convulsions and, in severe cases, collapse and death.

## Effects of Long-Term Overexposure in Humans

There are no reports of chronic poisoning from exposure to perchloric acid. Repeated skin contact causes drying, cracking and inflammation of the skin (dermatitis).

## Toxicity Data in Animals and Laboratory Tests

Lethal Dose Values

The poisoning strength of a compound can be estimated from the $LD_{50}$ obtained in animal tests. LD stands for lethal dose. The $LD_{50}$ is the amount of a chemical (weight of chemical per weight of animal) which is needed to kill one-half (50 percent) of the test animals. Test animals are usually rats, mice or other rodents. Routes of exposure are usually by mouth (oral) or through the skin (dermal). The following values are obtained for this material:[7]

$LD_{50}$ (rat, oral): 1,100 mg/kg
$LD_{50}$ (dog, oral): 400 mg/kg

Further general information on the $LD_{50}$ is available in the Centre's publication "What is an $LD_{50}$?"[8]

## IV. FIRE AND EXPLOSION HAZARDS

Perchloric acid is not combustible (does not burn), but it is a strong oxidizing agent, especially when heated to temperatures above 160°C (320°F). Combustible materials such as wood, paper and oil contaminated with perchloric acid become extremely flammable and can ignite spontaneously[9]. In one incident, perchloric acid spilled on a wooden floor instantly set the floor on fire. In another incident, spilled perchloric acid which was cleaned up with saw dust caused a minor explosion several hours after the residue was stored in a covered metal waste can. Further details on the explosive reactivity of perchloric acid can be found in Section V.

## V. CHEMICAL REACTIVITY

Perchloric acid is a very reactive chemical. It reacts vigorously with strong bases such as sodium hydroxide, perchloric acid also reacts with various other materials to form explosive compounds.

Most of the fires and explosions involving perchloric acid are the result of the accidental formation of 100% perchloric acid and its contact with organic material. Perchloric acid at 100% is dangerously unstable at room temperature. Under certain conditions, 100% perchloric acid is formed when a concentrated solution of the acid is mixed with a dehydrating agent such as sulfuric acid or phosphorus pentoxide or an excess of acetic anhydride at room temperature. Mixtures of perchloric acid and acetic anhydride are used in electropolishing. Serious explosions can occur during preparation of this mixture if special precautions are not taken[3].

The formation of highly unstable organic perchlorate compounds is also possible when perchloric acid is mixed with some solvents, particularly alcohols, ketones, glycols and glycol ethers[10-12]. Organic matter, when digested with hot perchloric acid, forms highly explosive organic perchlorates.

Organic perchlorates have been formed in unexpected ways. In one incident, an explosion occurred when a laboratory fume hood which was normally used for other chemical reactions was also used to exhaust hot perchloric acid. It was believed that the explosion was caused by reaction between perchloric acid and organic material previously deposited in the hood and duct[9]. In another report, there was a severe explosion during maintenance of a perchloric acid fume ventilation system[13]. The explosion was caused when the exhaust blower was struck with a chisel. This accident may have been due to a

shock-sensitive perchlorate derivative from the reaction of perchloric acid and the glycerine/lead oxide cement used in the assembly of the fume hood. Reactions with other laboratory chemicals which might have accumulated in the fume hood may also have contributed.

Hazardous reactions resulting in explosion can also occur when perchloric acid comes in contact with metals such as bismuth and antimony, fluorine gas, hydrogen halides (hydrogen fluoride, hydrogen chloride), sulfoxides and strong reducing agents. Mixing perchloric acid with water will generate heat[3,14,15].

Serious accidents can occur when exhausting perchloric acid vapours and mists. One way to minimize the chance of explosion is to design ventilation systems specifically to control perchloric acid vapours and mists. Information on design criteria for perchloric acid hoods is available in the literature[16,17] and from manufacturers of fume hoods. Details of special precautions to be taken during maintenance of perchloric acid ventilation systems are also available[3,18].

## VI. EXPOSURE LIMITS

Many Canadian jurisdictions have exposure limits similar to those established by the American Conference of Governmental Industrial Hygienists (ACGIH). The ACGIH has not recommended a Threshold Limit Value (TLV) for perchloric acid. Appropriate government agencies in each jurisdiction should be consulted to determine which regulations apply.

## VII. EXPOSURE CONTROLS

Engineering control methods to reduce hazardous exposures are preferred. Methods include mechanical (local exhaust) ventilation, process or personal enclosure, control of process conditions and process modification (for example, substitution of a less hazardous material).

Ventilation systems for exhausting perchloric acid mist and vapour must be specifically designed and maintained. Hoods designed for perchloric acid must only be used for this purpose and must be identified with large warning signs.

### Protective Clothing

Wear protective clothing such as gloves, coveralls and aprons as needed to prevent skin contact with perchloric acid. Not all materials provide protection, so it is important to use those which cannot be penetrated or

broken down by perchloric acid. Ensure impervious protective clothing is made of natural rubber, neoprene rubber, nitrile rubber, nitrile polyvinyl chloride or polyvinyl chloride. Wear splashproof chemical safety goggles for the eyes and a face shield (8-inch minimum) for the face, if the eyes or face are likely to come in contact with perchloric acid.

Immediately remove clothing contaminated with perchloric acid and immerse it in water. Discard or launder before re-use.

## Respiratory Protection

Wear approved respiratory protection if the airborne concentration of perchloric acid cannot be controlled. If respiratory protection is required, institute a complete respiratory protection program including selection, fit testing, training, maintenance and inspection. Refer to the CSA Standard Z94.4-M1982, "Selection, Care, and Use of Respirators," available from the Canadian Standards Association, Rexdale, Ontario, M9W 1R3.

The concentration of perchloric acid mist or vapour and the duration of exposure determine the degree of respiratory protection required. An air-purifying respirator suitable for acid mist may be acceptable. The respirator use limitations as specified by NIOSH/MSHA or the manufacturer must be observed.

Air-purifying respirators do not protect against oxygen-deficient atmospheres.

# VIII. STORAGE AND HANDLING

Use glass, ceramic or polyethylene containers for storage of perchloric acid solutions. Place containers inside or on a second container or tray to contain the acid in case of a break or spill.

Store closed containers in a clean, cool, well-ventilated area. Store perchloric acid separately from all other materials, preferably in a detached, non-combustible building marked clearly for this purpose.

Avoid generating mists when handling. Keep away from materials which can burn. Do not attempt to open a container of perchloric acid if its colour appears different from that of the pure substance.

Use the smallest possible amounts in designated areas with adequate ventilation, away from incompatible materials. Have emergency equipment readily available. Label all containers and keep containers closed when not in use. Empty containers may contain hazardous residues. When diluting or preparing solutions, always add the acid to water slowly to avoid boiling and splattering.

# IX. FIRST AID

## Inhalation

If symptoms are experienced, remove source of contamination or move victim to fresh air. Obtain medical advice immediately.

## Eye Contact

Immediately flush the contaminated eye(s) with lukewarm, gently flowing water for 30 minutes, holding the eyelid(s) open. Take care not to rinse contaminated water into a non-affected eye. Obtain medical attention immediately.

## Skin Contact

Avoid direct contact with the chemical. As quickly as possible, flush the contaminated area with lukewarm, gently running water for at least 20 minutes. Under running water, remove contaminated clothing. Obtain medical attention immediately.

## Ingestion

Never give anything by mouth if the victim is rapidly losing consciousness, or is unconscious or convulsing. Have the victim rinse the mouth thoroughly with water. DO NOT INDUCE VOMITING. Have victim drink 240 to 300 mL (8 to 10 oz.) of water. If vomiting occurs naturally, rinse the mouth and repeat the administration of water. Quickly transport the victim to an emergency facility.

## General

Provide supportive measures, comfort, warmth and rest. Consult a physician and/or the nearest Poison Control Centre for all exposures, except minor instances of inhalation or skin contact.

All first aid procedures should be periodically reviewed by a physician familiar with the substance and its conditions of use in the workplace.

## X. FIRE FIGHTING

Use water spray to fight fires involving perchloric acid. Move containers from the fire area if this can be done without risk. Use large quantities of water, but do not use water jets. Use water spray to cool containers to help prevent rupture. Water spray may also be used to reduce vapours.

## XI. CLEAN-UP AND DISPOSAL

Prepare an emergency action plan in advance. Provide appropriate training. Have emergency equipment readily available and in good working order. Restrict access to the area until completion of the clean-up. Ensure clean-up is conducted by trained personnel only. Extinguish or remove all ignition sources and ventilate the area. Notify government environmental agencies if the material is released into the environment.

Do not touch spilled material. Stop or reduce the leak if it is safe to do so. Prevent the material from entering sewers or confined spaces. Keep materials which can burn away from spilled material. Contain spill using non-combustible absorbent material such as sand or earth.

For small spills, neutralize the acid carefully by adding soda ash. Transfer the spilled liquid to a container of water for disposal. Keep the residue wet to prevent combustion upon drying. Flush the area well with water.

For large spills, contact police and emergency services and the supplier for advice.

To dispose of the waste, review federal, provincial and local government requirements. Disposal in a secure landfill may be acceptable.

# XII. REFERENCES

(1) Perchloric acid (solutions containing 50-72 per cent by weight perchloric acid in water) (Information sheets on hazardous materials; H53). London : Fire Prevention Information and Publications Centre, 1977. p. 45-46

(2) Rhees, R.C. Perchloric acid and perchlorates. In: Kirk Othmer encyclopedia of chemical technology. Vol. 5, Castor oil to chlorosulfuric acid. 3rd ed. New York; Toronto : John Wiley & Sons, 1979. p. 646-667

(3) Everett, K.; Graf, F.A., Jr. Handling perchloric acid and perchlorates. In: Steere, N.V., ed. CRC Handbook of laboratory safety. 2nd ed. Cleveland : The Chemical Rubber Co., 1971. p. 265-276

(4) Halton, D.M. How workplace chemicals enter the body. Hamilton, Ont. : CCOHS, 1985

(5) Acide perchlorique $HClO_4$ (Fiche toxicologique; no 141). Paris : INRS, 1982

(6) Perchloric acid. In: Weiss, G., ed. Hazardous chemicals data book. 2nd ed. Park Ridge, N.J. : Noyes Data Corporation, 1986. p. 820

(7) Selivanova, L.N.; Koltanova, I.G.; Vorobieva, E.N. On the general toxic effects of perchloric acid. Labor Hygiene and Occupational Diseases. Vol. 17, no. 8 (1973). p. 33-35 (summary)

(8) Bello, S.J.; Halton, D.M. What is an $LD_{50}$? Hamilton, Ont. : CCOHS, 1986

(9) Harris, E.M. Perchloric acid fires. Chemical Engineering. Vol. 56, no. 1 (Jan. 1949). p. 116-117

(10) Sweasey, D. Use of perchloric acid. Laboratory Practice. Vol. 17 (1968). p. 915

(11) Moureu, H.; Munsch, H. Mémoires originaux sur quelques accidents causés par la manipulation de l'acide perchlorique et des perchlorates. Archives des maladies professionnelles de médecine du travail et de sécurité sociale. Vol. 12, no. 2 (1951). p. 157-161

(12) Comas, S.M.; Palacin, R.G.; Vassallo, D. Hazards associated with perchloric acid-butylcellosolve polishing solutions. Metallography. Vol. 7 (1974). p. 47-57

(13) Boles, R.B. A system for safe handling of perchloric acid fumes. Air Engineering. (July 1967). p. 20-22

(14) Fire protection guide on hazardous materials. 9th ed. Quincy, Mass. : National Fire Protection Association, 1986

(15) Bretherick, L. Perchloric acid. In: Handbook of reactive chemical hazards. 2nd ed. London; Toronto : Butterworths, 1979. p. 777-787

(16) Perchloric acid hood data. In: Industrial ventilation : a manual of recommended practice. 18th ed. Lansing, Mich. : American Conference of Governmental Industrial Hygienists, 1984. p. 5-26

(17) Renton, L.N.; Duffield, G.A. Preliminary evaluation of an integral scrubber/fume hood design for control of noxious vapours. In: Goodfellow, H.D., ed. Ventilation '85. Amsterdam : Elsevier Science Publishers, 1986. p. 677-686

(18) Breysse, P.A. How to dismantle perchlorate contaminated lab exhaust systems : fire, explosion, and health hazards dictate extreme caution. Heating, Piping & Air Conditioning. (Aug. 1966). p. 126-127

Note: Additional references on this subject are available from CCOHS upon request.

## PLEASE NOTE

This summary was prepared at the Canadian Centre for Occupational Health and Safety (CCOHS) and is intended primarily as a source of information for persons who work with or may be occupationally exposed to this material. The information selected for inclusion is believed to be reliable and generally relevant to occupational health. Other information may be available which bears on particular work situations. The scientific data in many areas are limited and may allow a variety of interpretations. Additional information, corrections, comments and questions are welcome, and should be addressed to the Inquiries Service, CCOHS, 250 Main Street East, Hamilton, Ontario, L8N 1H6, (416) 572-2981; toll free 1-800-263-8276.

The information in this document was updated on February 27, 1987.